CHLORIDE-ASSISTED NITROLYSIS OF CYCLIC TERTIARY AMINES

Matthew D. Cliff

Aeronautical and Maritime Research Laboratory (AMRL)-DSTO, P.O. Box 1500, Salisbury, South Australia, 5108, Australia

Abstract - The synthesis of nitramines from tertiary amine heterocycles *via* a chloride-assisted nitrolysis is presented. The process is effective for heterocyclic systems containing a single tertiary amine moiety and gives good to excellent yields for primary, secondary and tertiary alkyl leaving groups. Heterocyclic systems containing two tertiary amines are best nitrated *via* a *tert*-butyl leaving group, with other alkyl moieties leading to ring-opened species upon treatment with nitrating media both in the presence and absence of chloride ions.

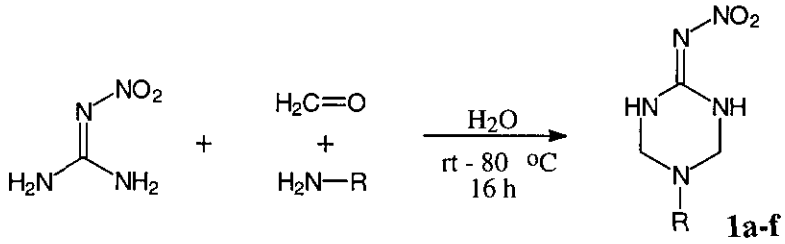
The use of chloride ions to assist in the nitration of secondary amines was extensively investigated in the middle of this century by Wright *et al.*[1] Using this technique, chloride ions are oxidised to 'electropositive' chloride (Cl^+) by nitric acid.[1d,e] The electropositive chloride then converts the secondary amine to the corresponding chloramine, which is less basic than the parent amine, and finally the nitramine is formed following electrophilic attack by a nitronium ion.[1e,2] Typical chloride ion sources include NH_4Cl, HCl, $ZnCl_2$ and acetyl chloride.[2,3] Reaction media normally used include nitric acid/acetic anhydride mixtures in which Cl^+ is stabilised as chloride acetate (ClOAc), or neat nitric acid.[1e,2]

Despite the success of chloride-assisted nitramine formation from secondary amines, very little work has appeared in the open literature since the late 1940's. A recent communication from these laboratories demonstrated the advantageous use of chloride-assisted nitrolysis of a tertiary amine to form an energetic nitramine.[4] This previously unreported route was used to form the patented nitramine 2-nitroimino-5-nitrohexahydro-1,3,5-triazine.[5] The aim of this paper is to present a more detailed study of chloride-assisted nitramine formation. To investigate this fully, a range of alkyl leaving groups was trialed with three mono and di(*tert*-amine) cyclic substrates.

Previous work has shown that NH_4Cl in neat HNO_3 provides optimal yields of the target nitramine.[4] Metal chloride sources such as copper, tin and lead chloride were not used to avoid the risk of forming

compounds possessing primary explosive properties. The tertiary amines (**1a-f**) were formed *via* a Mannich condensation[6,7] of nitroguanidine, formaldehyde and the appropriate primary amine in 83-89% yield (Scheme 1).

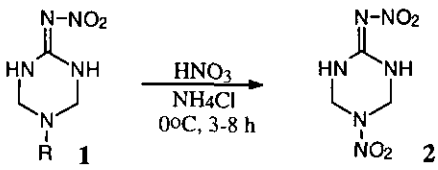
Scheme 1



1a R = *tert*-butyl (87%) **d** R = benzyl (84%)
b R = *iso*-propyl (89%) **e** R = *n*-butyl (83%)
c R = cyclohexyl (89%) **f** R = *n*-propyl (83%)

A series of comparative nitrations were carried out at 0°C to investigate the effect of various leaving groups, with all chloride-assisted reactions using 1.05 molar equivalence NH_4Cl (Table 1). The previously reported *tert*-butyl protected species[4] afforded the highest yield of target nitramine (**2**) (89%) and showed the greatest enhancement of product yield for all mono-protected species. The *iso*-propyl (**1b**) and cyclohexyl (**1c**) substrates gave the final nitrated species both in the presence and absence of NH_4Cl. Formation of **2** from **1b** and **1c** in the absence of NH_4Cl was unexpected and is not seen with any other alkyl leaving group. A suitable explanation for these results is not available at this stage. The use of NH_4Cl in the reaction mixture, however, resulted in enhanced yields of **2** from both amines (51% and 75% respectively) and cleaner, non-exothermic reactions. The efficacy of the chloride ion was clearly demonstrated for the *n*-butyl and *n*-propyl species (**1e**) and (**1f**). Nitrolysis carried out at 0°C in neat nitric acid failed to give the target nitramine and resulted in recovery of the starting tertiary amines upon work-up. In the presence of NH_4Cl, however, nitramine (**2**) was isolated in 59% and 68% yields from **1e** and **1f** respectively. The use of primary alkyl leaving groups involved longer reaction times and typically took 8 hours to complete at 0°C as opposed to 2-3 hours for secondary and tertiary alkyl moieties. Nitramine (**2**) was able to be isolated from **1e** and **1f** in neat nitric alone by allowing the reaction to proceed at 20°C, however, product yields were significantly lower. Warming to 40°C resulted in a further reduction of yield, with evidence of product decomposition by ^1H NMR. Nitrolysis of the benzyl protected species (**1d**) resulted in benzyl decomposition products only being isolated, with no evidence of **2** or the starting amine being present.

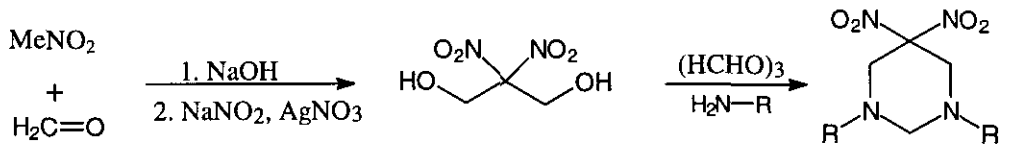
Table 1. Effect of NH_4Cl inclusion on the synthesis of **2**.



Amine	*Yield 2 (%), HNO_3*			*Yield 2 (%)*
	0°C	**20°C**	**40°C**	*NH_4Cl, HNO_3*
1a	0			89
1b	27			51
1c	67			75
1d	-			-
1e	0	28	13	59
1f	0	39	20	68

The effectiveness of chloride-assisted nitrolysis for dinitramine formation was investigated for the target 1,3,5,5-tetranitrohexahydropyrimidine (**3**), a patented oxidant used in explosive and rocket propellant compositions.[8] Diol (**4**) was formed by condensation of nitromethane and formaldehyde. Ag^+ induced oxidation of sodium nitrite was used to form the nitronium ion *in situ* to quench the carbanion and gave **4** in 52% yield (Scheme 2).[9,10]

Scheme 2



4 (52%)

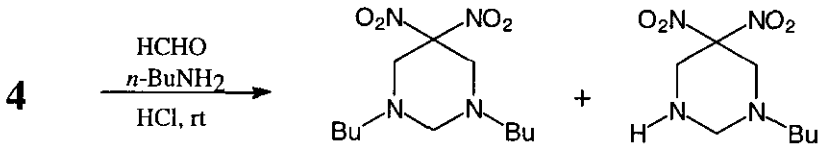
5a-c

5a R = *tert*-butyl (52%)
b R = *iso*-propyl (86%)
c R = cyclohexyl (93%)

Condensation of **4** with depolymerised paraformaldehyde and primary amines (such as *tert*-butylamine, *iso*-propylamine and cyclohexylamine) gave the cyclic diamines (**5a-c**) in 52, 86 and 93% yields

respectively. Synthesis of the *n*-butyl substrate was achieved using aqueous formaldehyde to give **5d** in 49% yield, with the mono-butyl adduct (**6**) also isolated in 18% yield (Scheme 3).[11]

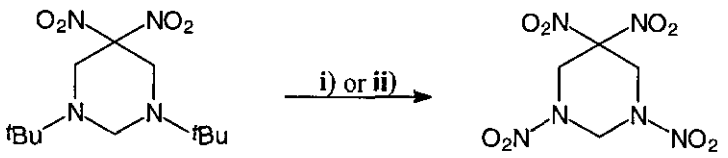
Scheme 3



5d (49%) **6** (18%)

Nitrolysis of *tert*-butyl (**5a**) at 0°C in neat nitric acid and 1.05 molar equivalence NH_4Cl gave the target nitramine (**3**) in 76% yield. Absence of the electropositive chloride species resulted in an inferior yielding reaction, with **3** isolated in 35% yield (Scheme 4).

Scheme 4

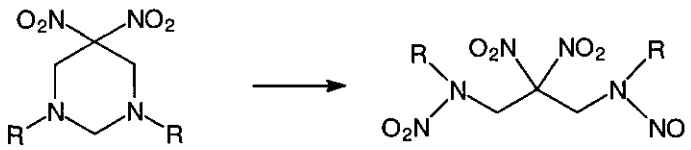


5a **3**

i) NH_4Cl, HNO_3 (76%)
ii) HNO_3 (35%)

The dialkyl protected substrates (**5b, c**) failed to give **3** in nitric acid concentrations ranging from 90-100% and 1.05 molar equivalence of NH_4Cl, the products instead being the ring-opened linear nitrosamines (**7a, b**) (Scheme 5). The presence or otherwise of electropositive chloride had little effect on the yields of **7** obtained and failed to effect the synthesis of **3** (Table 2). Treatment of **5d** under the range of conditions utilised for **5b, c** above resulted in the isolation of an inseparable mixture of **7c** and a second, unidentified ring-opened species. Levins *et al.*[11] reported the formation of ring-opened compounds including **7** from **5a-d** using nitric acid media at concentrations ranging from 95-100% during their attempts to form **3**. The synthesis of **3** in poor yield from **5b** is reported[11] using 90% nitric acid, however, this reaction was unable to be reproduced in these laboratories, with **7a** the only identifiable product isolated.

Scheme 5



5b-d

7a R = *iso*-propyl
b R = cyclohexyl
c R = *n*-butyl

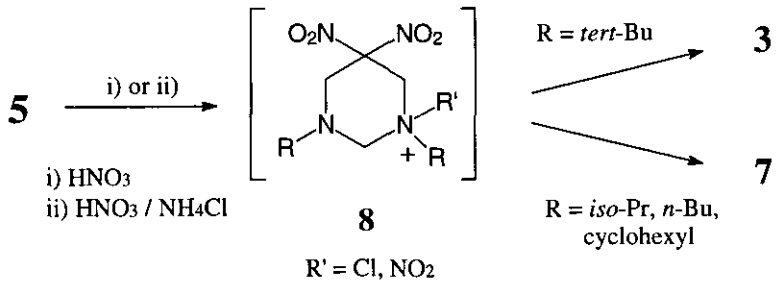
Table 2: Yield **7** under various nitrolysis conditions

Amine	*HNO_3, NH_4Cl*		*HNO_3*	
	Acid Conc (%)	*Yield*	*Acid Conc.(%)*	*Yield*
5b	100	**7a**, 70%	100	**7a**, 70%
5b	90	**7a**, 4%	90	**7a**, 14%
5c	100	**7b**, 92%	100	**7b**, 95%
5c	90	**7b**, 9%	90	**7b**, 9%

Reactions carried out at 0°C for 3 hours.

Treatment of **5** with either NH_4Cl/HNO_3 or nitric acid (90-100%) leads to the intermediate carbocation (**8**), with labile groups such as *tert*-butyl leading ultimately to **3**. Poorer leaving groups such as *iso*-propyl (**5b**), cyclohexyl (**5c**) and *n*-butyl (**5d**) lead instead to series (**7**), with none of the target nitramine (**3**) formed (Scheme 6).

Scheme 6



i) HNO_3
ii) HNO_3 / NH_4Cl

8

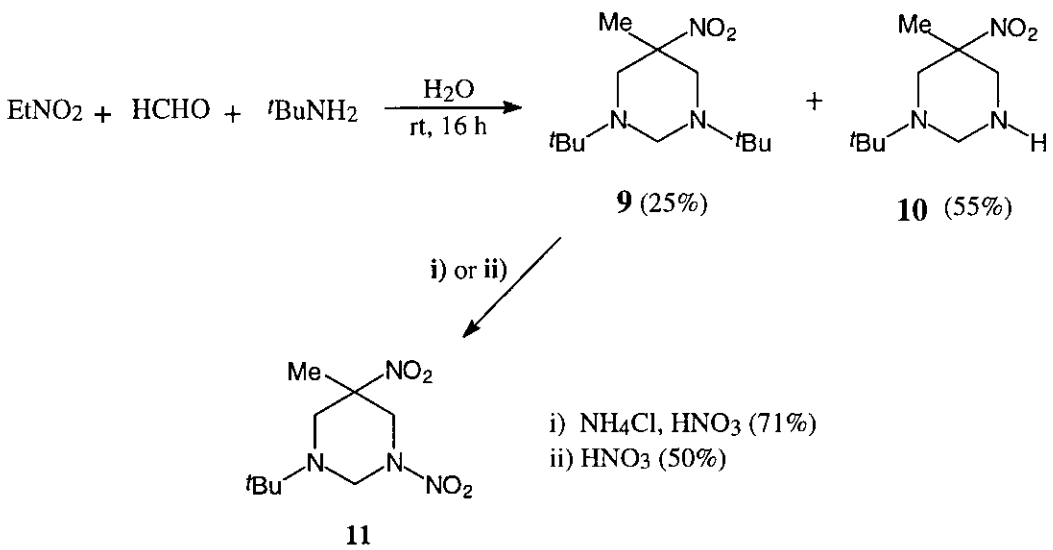
R' = Cl, NO_2

R = *iso*-Pr, *n*-Bu, cyclohexyl

Nitration of **5b, c** was attempted using a number of nitrolysis methods including Ac_2O/HNO_3 and $(CF_3COO)_2O/HNO_3$ in the presence and absence of NH_4Cl. All experiments resulted in either isolation of the ring-opened species (**7a, b**) or total decomposition of the ring system.

A second cyclic diamine (**9**) was synthesised in a one-pot method from nitroethane, formaldehyde and *tert*-butylamine in 25% yield, with the secondary amine (**10**) isolated as the major product in 55% yield (Scheme 7).[12] Treatment of **9** with neat nitric acid gave the mononitramine (**11**) in 50% yield. Addition of NH_4Cl to the system resulted in an increase in yield to 71%. In both cases conversion to the dinitramine was unable to be achieved. Despite being structually similar, *tert*-amines (**5a**) and (**9**) lead to different nitrolysis products. The fact that **5a** undergoes two nitrolysis reactions while **9** only participates in a single reaction can be explained on the basis of differences in basicity of the *tert*-butylamines. The lack of reactivity of the second amine moiety of **9** is presumably due to protonation of the amine site, thereby preventing attack by NO_2^+. Previous work on the nitrolysis of **5a** and **9** has shown good results using H_2SO_4/HNO_3 and neat nitric acid respectively. Use of a chloride catalysed nitrolysis, however, allowed the reactions to proceed at either lower temperature (0°C as opposed to 45°C) or shorter reaction periods.[12]

Scheme 7



In summary, the effectiveness of chloride-assisted nitrolysis for the formation of cyclic nitramines has been demonstrated. The process is most suitable for heterocycles containing a single tertiary amine site, with primary, secondary and tertiary alkyl leaving groups giving good to excellent yields. Nitrolysis of

heterocyclic systems containing two tertiary amine moieties have shown enhanced yields for a *tert*-butyl leaving group only, with all other moieties proving ineffective in the trialed substrates.

ACKNOWLEDGMENTS

The author wishes to thank Mr Mark Fitzgerald for his assistance and Dr Ian Dagley for valuable discussions.

EXPERIMENTAL SECTION

CAUTION: Compounds (**2**, **3**, **4**) and (**7**) are sensitive explosives and should not be subjected to impact, friction, electrostatic discharge or high temperatures Fume cupboards rated for explosives synthesis should be used along with appropriately trained personell. Compound (**1a**) was synthesised according to Cliff *et al.*[4] Nmr spectra were recorded on a Varian Unity 300 Fourier Transform NMR spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 300 MHz and 75.6 MHz respectively. Chemical shifts are reported as δ values in ppm and are relative to internal TMS. Melting points were determined on an Electrothermal IA 9200 melting point apparatus and are uncorrected. Low resolution MS spectra were recorded on an Electrospray Ionisation VG Quattro spectrometer with a cone voltage of 30-60 V. High resolution MS spectra were recorded on an Electrospray Ionisation VG AutoSpec with cone voltage 20-50 V, skimmer offset +10 V and a resolution of 2.5 K. All MS samples were infused in 50% *MeOH*/H_2O. Elemental analyses were performed by the National Analytical Laboratories Pty Ltd, Victoria, Australia. All samples were dried at 30°C (0.01 mmHg) for 24 h over P_2O_5 prior to elemental analysis. Spectral and analytical data is presented for previously reported compounds where literature data is inadequate.

2-Nitroimino-5-(*iso*-propyl)hexahydro-1, 3, 5-triazine (1b)

General Procedure

To a slurry of nitroguanidine (5.0 g, 48 mmol) in H_2O (20 mL) was added a 37% aqueous formaldehyde solution (8.8 mL, 82 mmol) and the mixture stirred for 30 min at rt. *Iso*-propylamine (3.4 g, 57.6 mmol) was then added slowly and the mixture stirred for 1 h at rt and 16 h at 80°C. The slurry was cooled to rt, filtered and the solid washed with cold water and dried to give a white powder. Recrystallisation from acetone gave the title compound as white crystalline plates (6.8 g, 89%), mp 191-192°C.

^{1}H NMR (DMSO-d_6) δ 8.89 (2H, s, 2xNH), 4.33 (4H, s, 2 x CH_2), 2.88 (1H, sept, J = 6.5 Hz, $C\underline{H}(CH_3)_2$), 1.09 (6H, d, J = 6.3 Hz, 2 x CH_3); ^{13}C NMR (DMSO-d_6) δ 156.1 (C=N), 57.8 (2xCH_2), 47.3 (CH), 20.8 (2xCH_3); IR (KBr) 3330, 3204, 3123, 2976, 1588 (NO_2), 1462, 1304 cm^{-1}; MS (ES+ve) *m/z* 188 ($M+H^+$,

100), 172 (M-CH_3^+, 4), 143 (13); Anal. Calcd for $C_6H_{13}N_5O_2$: C, 38.50; H, 7.00; N, 34.41. Found: C, 38.89; H, 7.36; N, 37.70.

5-Cyclohexyl-2-nitroiminohexahydro-1, 3, 5-triazine (1c)

Using the general procedure described above for the synthesis of **1b** with a reaction time of 72 h at ambient temperature, the title compound was obtained as a white powder (89%) after recrystallisation from acetone, mp 190-191°C.

^{1}H NMR (DMSO-d_6) δ 8.85 (2H, s, 2xNH), 4.35 (4H, s, 2xCH_2), 2.59-2.50 (1H, m, CH), 1.90-1.54 (4H, m, 2xCH_2), 1.28-1.10 (6H, m, 3xCH_2); ^{13}C NMR (DMSO-d_6) δ 156.2 (C=N), 57.1 (2xCH_2), 55.1 (CH), 30.5 (2xCH_2), 25.3 (CH_2), 24.5 (2xCH_2); IR (KBr) 3343, 3312, 3200, 2925, 2853, 1593 (NO_2), 1474, 1382, 1299, 1248, 1108 cm^{-1}; MS (ES+ve) *m/z* 228 (M+H^+, 100), 183 (19); Anal. Calcd for $C_9H_{17}N_5O_2$: C, 47.50; H, 7.54; N, 30.82. Found: C, 47.10; H, 7.80; N, 30.60.

5-Benzyl-2-nitroiminohexahydro-1, 3, 5-triazine (1d)

Using the general procedure described above for the synthesis of **1b** with a reaction time of 72 h at ambient temperature, the title compound was obtained as white, crystalline needles (84%) after recrystallisation from acetone, mp 217-218°C.

^{1}H NMR (DMSO-d_6) δ 8.77 (2H, s, 2xNH), 7.43-7.28 (5H, m, 5xAr-H), 4.24 (4H, s, 2xCH_2), 3.79 (2H, s, C$\underline{H_2}$Ph); ^{13}C NMR (DMSO-d_6) δ 155.5 (C=N), 137.4 (Ar-C1), 128.7 (Ar-C3, 5), 128.3 (Ar-C1, 6), 127.4 (Ar-C4), 59.3 (2xCH_2), 53.7 ($\underline{C}H_2$Ph); IR (KBr) 3356, 3194, 3120, 2359 (w), 1594 (NO_2), 1481, 1310, 1244, 1109 cm^{-1}; MS (ES+ve) *m/z* 236 (M+H^+,100), 191 (19); Anal. Calcd for $C_{10}H_{13}N_5O_2$: C, 51.06; H, 5.57; N, 29.77. Found: C, 50.72; H, 5.29; N, 29.64.

5-Butyl-2-nitroiminohexahydro-1, 3, 5-triazine (1e)

Using the general procedure described above for the synthesis of **1b** with a reaction time of 72 h at ambient temperature, the title compound was obtained as white, crystalline needles (83%) after recrystallisation from acetone, mp 181-183°C.

^{1}H NMR (DMSO-d_6) δ 8.68 (2H, s, 2xNH), 4.24 (4H, s, 2xCH_2), 2.56 (2H, t, *J* = 7.2 Hz, NCH_2), 1.46-1.26 (4H, m, CH_2CH_2), 0.89 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (DMSO-d_6) δ 155.6 (C=N), 59.7 (2xCH_2), 49.2 (NCH_2), 29.3 ($\underline{C}H_2CH_2CH_3$), 19.6 ($\underline{C}H_2CH_3$), 13.8 (CH_3); IR (KBr) 3349, 3203, 3124, 2929, 1601, 1313, 1104 cm^{-1}; MS (ES+ve) *m/z* 202 (M+H^+,100), 186 (M-CH_3^+, 6), 157 (23); Anal. Calcd for $C_7H_{15}N_5O_2$: C, 41.78; H, 7.51; N, 34.80. Found: C, 41.90; H, 7.80; N, 34.90.

2-Nitroimino-5-propylhexahydro-1, 3, 5-triazine (1f)

Using the general procedure described above for the synthesis of **1b**, the title compound was obtained as white, crystalline needles (83%) after recrystallisation from acetone, mp 196-198°C.

^{1}H NMR (DMSO-d_6) δ 8.89 (2H, s, 2xNH), 4.24 (4H, s, 2xCH_2), 2.55-2.51 (2H, m, NCH_2), 1.51-1.43 (2H, m, $C\underline{H}_2CH_3$), 0.88 (3H, t, J = 7.1 Hz, CH_3); ^{13}C NMR (DMSO-d_6) δ 156.0 (C=N), 59.7 (2xCH_2), 51.5 (NCH_2), 20.4 ($\underline{C}H_2CH_3$), 11.4 (CH_3); IR (KBr) 3339, 3203, 3126, 2956, 1613 (NO_2), 1348, 1319, 1238, 1107 cm^{-1}; MS (ES+ve) *m/z* 188 ($M+H^+$, 100), 172 ($M-CH_3^+$, 11), 143 (53); Anal. Calcd for $C_6H_{13}N_5O_2$: C, 38.50; H, 7.00; N, 37.41. Found: C, 38.56; H, 6.60; N, 37.77.

5-Nitro-2-nitroiminohexahydro-1, 3, 5-triazine (2)

General Nitration Procedure for Amines 1b, c, e, f.

To 100% nitric acid (3.0 mL) at 0°C was added amine (**1b**) (500 mg, 2.67 mmol) over a 10 min period. Ammonium chloride (150 mg, 2.80 mmol) was then added and the resulting yellow solution was stirred at 0°C for 3 h and poured onto ice (10 g). The precipitated solid was stirred for 1 h at rt until the aqueous phase became clear and then chilled to 0°C, filtered, washed with cold water and dried *in vacuo* to give pure **2** as a white solid (260 mg, 51%), mp 205-206°C. Spectral data was consistent with that previously reported by Cliff *et al.*[4]

1, 3, 5, 5-Tetranitrohexahydropyrimidine (3)

To neat nitric acid (4.0 mL) at 0°C was added the cyclic amine (**5a**) (400 mg, 1.39 mmol) over a 10 min period. Ammonium chloride (78 mg, 1.46 mmol) was then added and the resulting solution was stirred at 0°C for 2 h and then poured onto ice (7 g). The precipitated solid was filtered, washed with cold water and dried *in vacuo* to give pure **3** as a white solid (280 mg, 76%), mp 150-151°C.

^{1}H NMR (acetone-d_6) δ 6.31 (2H, s, NCH_2N), 5.47 (4H, s, 2xCH_2); ^{13}C NMR (acetone-d_6) δ 107.7 ($C(NO_2)_2$), 60.0 (NCH_2N), 49.7 (2xCH_2); IR (KBr) 3034, 1576 (NO_2), 1547 (NO_2), 1380, 1295, 994, 894 cm^{-1}; MS (ES+ve) *m/z* 250 ($M-O^+$, 4), 219 ($M-NO_2^+$, 16), 174 (20), 159 (100); HRMS calcd for $C_4H_6N_6O_7$ 250.0298, found 250.0299.

2, 2-Dinitro-1, 3-propanediol (4)

The title compound was synthesised by the procedure of Borgardt *et al.*[10] Recrystallisation from ether/CH_2Cl_2 gave the diol as a light yellow solid (52%), mp 134-135°C.

^{1}H NMR ($CDCl_3$) δ 4.57 (4H, s, 2xCH_2), 2.60 (2H, s(b), 2xOH); ^{13}C NMR (DMSO-d_6) δ 119.1 ($C(NO_2)_2$), 60.1 (2 x CH_2); IR (KBr) 3280 (OH), 1587, 1569 (NO_2), 1350, 1320, 1069 cm^{-1}; MS (ES+ve) *m/z* 135 (M-CH_2OH^+, 100), 105 (19), 59 (10).

1, 3-Di(*tert*-butyl)-5, 5-dinitrohexahydropyrimidine (5a)

General Procedure[9]

To a solution of **4** (5.50 g, 33.1 mmol) in methanol (6 mL) at 0°C was slowly added *tert*-butylamine (4.76 g, 65.2 mmol) in methanol (6 mL). The ice bath was removed and the mixture was allowed to stir at rt for 30 min then cooled to 0°C and a methanolic solution of depolymerised paraformaldehyde added (effected by refluxing paraformaldehyde (1.15 g, 36 mmol) and potassium carbonate (4 mg) in absolute methanol (10 mL) for 24 h). The reaction was warmed to rt for 30 min and then heated to reflux for 4 h. The solution was chilled to 0°C for 24 h and the resulting solid was collected and washed with cold methanol to give the title compound as an off-white crystalline solid (4.85 g, 52%), mp 77-78°C.

^{1}H NMR (acetone-d_6) δ 3.69 (4H, s, 2xCH_2), 3.61 (2H, s, NCH_2N), 1.14 (18H, s, 2x$C(CH_3)_3$); ^{13}C NMR (acetone-d_6) δ 116.0 ($C(NO_2)_2$), 63.9 (2xCH_2), 54.5 (NCH_2N), 51.6 (2x$\underline{C}(CH_3)_3$), 26.4 (2x$C(\underline{C}H_3)_3$); IR (KBr) 2973, 1564 (NO_2), 1366, 1206, 1036 cm^{-1}; MS (ES+ve) *m/z* 289 (M+H^+, 100), 244 (8), 171 (39); HRMS calcd for $C_{12}H_{25}N_4O_4$ 289.1876, found 289.1863.

1, 3-Di(*iso*-propyl)-5, 5-dinitrohexahydropyrimidine (5b)

Using the general procedure described above for the synthesis of **5a**, the title compound was obtained as a yellow oil (86%) after purification by column chromatography (4% ethyl acetate/hexane).

^{1}H NMR ($CDCl_3$) δ 3.58 (4H, s, 2xCH_2), 3.46 (2H, s, CH_2), 2.97 (2H, sept, *J* = 6.6 Hz, 2xCH), 1.09 (2x6H, d, *J* = 6.6 Hz, 2xCH($C\underline{H}_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 113.4 ($C(NO_2)_2$), 69.3 (NCH_2N), 52.4 (2xNCH_2), 51.3 (2xCH), 18.4 (4 x CH_3); IR (neat) 2968, 1580 (NO_2), 1463, 1322, 1238, 1103 cm^{-1}; MS (EI+ve) *m/z* 259 (M-H^+, 13), 213 (M-HNO_2^+, 10), 196 (24), 183 (35), 157 (20), 114 (100); HRMS calcd for $C_{10}H_{19}N_4O_4$ 259.1407, found 259.1404.

1, 3-Dicyclohexyl-5, 5-dinitrohexahydropyrimidine (5c)

Using the general procedure described above for the synthesis of **5a**, the title compound was obtained as a yellow oil (93%) after purification by column chromatography (10% ethyl acetate/hexane). The oil solidified on standing to give a light yellow solid, mp 81-82°C.

^{1}H NMR ($CDCl_3$) δ 3.62 (4H, s, 2xCH_2), 3.54 (2H, s, NCH_2N), 2.54-2.47 (2H, m, 2xCH), 1.84- 1.10 (20H, m, 10xCH_2); ^{13}C NMR ($CDCl_3$) δ 113.5 ($C(NO_2)_2$), 69.1 (NCH_2N), 61.2 (2 x NCH_2), 52.3 (2xCH),

29.1 (4xCH_2), 25.9 (2xCH_2), 25.5 (4xCH_2); IR (KBr) 2935, 2848, 1576 (NO_2), 1440, 1098 cm^{-1}; MS (EI+ve) *m/z* 339 ($M-H^+$, 39), 294 ($M-NO_2^+$, 22), 276 (32), 247 (10), 141 (18), 112 (18); HRMS calcd for $C_{16}H_{27}N_4O_4$ 339.2033, found 339.2032.

1, 3-Dibutyl-5, 5-dinitrohexahydropyrimidine (5d) and 1-butyl-5, 5-dinitroheptahydropyrimide (6)

The title compounds were synthesised by the procedure of Levins *et al.*[11] Purification by column chromatography (5% ethyl acetate/hexane) gave **5d** as a light orange oil (49%) and **6** as a light yellow oil (18%).

5d ^1H NMR ($CDCl_3$) δ 3.66 (4H, s, 2xCH_2), 3.40 (2H, s, NCH_2N), 2.53 (2x2H, t, J = 7.3 Hz, 2xNCH_2), 1.55-1.22 (2x4H, m, 2xCH_2CH_2), 0.92 (2x3H, t, J = 7.2 Hz, 2xCH_3); ^{13}C NMR ($CDCl_3$) δ 112.4 ($\underline{C}(NO_2)_2$), 73.2 (NCH_2N), 55.8 (2xCH_2), 53.7 (2xCH_2), 29.0 (2x$NCH_2\underline{C}H_2$), 20.2 (2x$\underline{C}H_2CH_3$), 13.9 (2xCH_3); IR (neat) 2958, 2932, 2870, 1576 (NO_2), 1466, 1320, 1211, 1100 cm^{-1}; MS (EI+ve) *m/z* 287 ($M-H^+$, 21), 242 ($M-NO_2^+$, 100); HRMS calcd for $C_{12}H_{24}N_3O_2$ 242.1869, found 242.1869.

6 ^1H NMR ($CDCl_3$) δ 4.62 (2H, s, CH_2), 4.41 (2H, s, CH_2), 4.03 (2H, s, CH_2), 2.63 (2H, t, J = 7.2 Hz, $C\underline{H}_2CH_2$), 1.48-1.24 (4H, m, $C\underline{H}_2C\underline{H}_2$), 0.90 (3H, t, J = 7.0, CH_3); ^{13}C NMR ($CDCl_3$) δ 109.4 ($C(NO_2)_2$), 83.6 (NCH_2N), 69.1 (CH_2), 54.2 (CH_2), 51.2 (CH_2), 29.7 ($NCH_2\underline{C}H_2$), 19.9 ($\underline{C}H_2CH_3$), 13.8 (CH_3); IR (neat) 2959, 2871, 1576 (NO_2), 1444, 1350, 1317, 1209 cm^{-1}; MS (EI+ve) *m/z* 233 ($M+H^+$, 8), 190 (100), 144 (38), 98 (38).

***N, N'*-Di(*iso*-propyl)-*N*-nitro-*N'*-nitroso-2, 2-dinitropropyl-1, 3-diamine (7a)**

General Procedure

To neat HNO_3 (4.0 mL) at 0°C was added *iso*-propylamine **5b** (300 mg, 1.15 mmol) in a single addition. Solid NH_4Cl (65 mg, 1.21 mmol) was added and the resulting yellow solution was stirred for 3 h at 0°C. The solution was poured onto ice (6 g), filtered and the solid was washed with cold water and dried to give the title compound as a white powder (260 mg, 70%), mp 106-108°C (explosive decomp.).

^1H NMR ($CDCl_3$) δ 4.71 (2H, s, CH_2), 4.61 (2H, s, CH_2), 4.57-4.37 (2H, m, 2xCH), 1.60 (6H, d, J = 6.7 Hz, $CH(C\underline{H}_3)_2$), 1.39 (6H, d, J = 6.8 Hz, $CH(C\underline{H}_3)_2$); ^{13}C NMR ($CDCl_3$) δ 116.4 ($C(NO_2)_2$), 57.9 (CH_2), 57.2 (CH_2), 51.8 (CH), 46.2 (CH), 22.3 (2xCH_3), 18.9 (2 x CH_3); IR (KBr) 3009, 2977, 2940, 1584, 1567, 1546, 1468, 1384, 1280 cm^{-1}; MS (EI+ve) *m/z* 322 (M^+, 5), 280 (39), 143 (56), 127 (39); HRMS calcd for $C_9H_{18}N_6O_7$ 322.1236, found 322.1231.

N, N'-Dicyclohexyl-N-nitro-N'-nitroso-2, 2-dinitropropyl-1, 3-diamine (7b)

Using the general procedure described above for the synthesis of **7a**, the title compound was obtained as a white solid (92%), mp 136°C (explosive decomp.).

^{1}H NMR (acetone-d_6) δ 5.02 (2H, s, CH_2), 4.87 (2H, s, CH_2), 4.34-4.12 (2H, m, 2xCH), 2.26-1.21 (20H, m, 2x$(CH_2)_5$); ^{13}C NMR (acetone-d_6, In part) δ 65.8 (CH_2), 64.9 (CH_2), 53.0 (CH), 47.3 (CH), 33.6 (2 x CH_2), 26.2 (2 x CH_2), 26.1 (2 x CH_2), 25.7 (CH_2), 25.5 (CH_2); IR (KBr) 2932, 2856, 1534, 1571, 1560, 1425, 1282, 1080 cm^{-1}; MS (LSIMS) *m/z* 403 (M+H$^+$, 18), 373 (11), 183 (76), 107 (34), 83 (100); HRMS calcd for $C_{15}H_{27}N_6O_7$ 403.1942, found 403.1955.

1, 3-Di(*tert*-butyl)-3-methyl-3-nitrohexahydropyrimidine (9) and

1-(*tert*-butyl)-3-methyl-3-nitroheptahydropyrimidine (10)

To a solution of nitroethane (3.0 g, 40 mmol) in MeOH (20 mL) at 0°C was slowly added an aqueous solution of 36% formaldehyde (8.0 mL) followed by *tert*-butylamine (2.78 g, 38 mmol). The mixture was warmed to rt and stirred for 16 h before cooling to 0°C. The precipitated solid was collected by filtration, dried and purified by column chromatography (10% ethyl acetate/hexane) to give **9** (1.20 g, 25%, mp 115-116°C) and **10** (2.06 g, 55%, mp 79-80°C) as white, crystalline solids.

9 ^{1}H NMR ($CDCl_3$) δ 3.87 (1H, d, *J* = 8.3 Hz), 3.64 (2H, d, *J* = 11.8 Hz), 2.91 (1H, d, *J* = 8.3 Hz), 2.35 (2H, d, *J* = 11.7 Hz), 1.50 (3H, s, CH_3), 1.10 (9H, s, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 85.6 ($\underline{C}(CH_3)NO_2$), 63.9, 53.5, 27.5, 26.3 ($C(\underline{C}H_3)_3$), 24.1; IR (KBr) 2971, 2874, 2825, 2751, 2702, 1540 (NO_2), 1450, 1348, 1212, 1048 cm^{-1}; MS (ES+ve) *m/z* 258 (M+H$^+$, 100); HRMS calcd for $C_{13}H_{28}N_3O_2$ 258.2182, found 258.2177.

10 ^{1}H NMR ($CDCl_3$) δ 4.60 (2H, dt, *J* = 2.0, 7.6 Hz), 3.95 (1H, d, *J* = 7.9 Hz), 3.82 (1H, dt, *J* = 2.0, 12.3 Hz), 3.47 (1H, d, *J* = 12.4 Hz), 2.59 (1H, d, *J* = 12/3 Hz), 1.46 (3H, s, CH_3), 1.09 (9H, s, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 84.5, 81.2, 71.5, 53.1, 52.7, 26.5, 21.6; IR (KBr) 2974, 2877, 2824, 2774, 1540 (NO_2), 1470, 1349, 1235, 1168, 1087, 1028 cm^{-1}; MS (ES+ve) *m/z* 203 (M + 2H$^+$, 100%), 191 (8%), 147 (37%).

1-(*tert*-Butyl)-3-methyl-3, 5-dinitrohexahydropyrimidine (11)

To 98% HNO_3 (4.0 mL) at 0°C was added NH_4Cl (66 mg 1.22 mmol) and the resulting solution stirred for 5 min. Amine (**9**) (250 mg, 0.97 mmol) was added slowly over a 10 min period and the mixture stirred at 0°C for 2 h. The mixture was then poured onto ice (8 g) and the resulting precipitate collected to give the title compound as a white solid (170 mg, 71%), mp 115-116°C.

^{1}H NMR (acetone-d_6) δ 5.53 (1H, dt, *J* = 1.6, 11.7 Hz), 5.40 (1H, dt, *J* = 1.6, 15.1 Hz), 4.15 (1H, d, *J* = 11.8 Hz), 3.95 (1H, dt, *J* = 1.9, 12.9 Hz), 3.86 (1H, d, *J* = 15.2 Hz), 1.66 (3H, s, CH_3), 1.21 (9H, s,

$C(CH_3)_3$); ^{13}C NMR (acetone-d_6) δ 86.2, 63.8, 54.3, 52.6, 26.3, 25.5, 22.6; IR (KBr) 2977, 2542, 1556 (b), 1384 (b), 1183, 1013, 881 cm^{-1}; MS (ES+ve) *m/z* 247 ($M+H^+$, 100), 200 ($M-NO_2^+$, 9), 191 (46); HRMS calcd for $C_9H_{19}N_4O_4$ 247.1406, found 247.1405.

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Received, 13th October, 1997